GOVERNMENT OF INDIA, THE PATENT OFFICE
214, ACHARYA JAGADISH BOSE ROAD
CALCUTTA-700017.

Complete Specification No. 158902 dated 11th February, 1983.

Application No. 38/DEL/1983 dated 11th February, 1983.

Acceptance of the complete specification advertised on 14th February, 1987

Index at acceptance — 32 E [IX (1)]

International Classification — C 08 F 3/50.

A PROCESS FOR THE PREPARATION OF POLYETHYLENE TEREPHTHALATE FROM POLY (ETHYLENE TEREPHTHALATE) WASTE.

SIR PADAMPAT RESEARCH CENTRE, A Division of J.K. Synthetics Limited, Jaykaynagar, Kota-324 003, Rajasthan, India, an Indian Centre.

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :-

PRICE : TWO RUPEES

This invention relates to a process for the preparation of polyethylene terephthalate from ~~xxxxxxxxxx~~ poly(ethylene terephthalate) waste to prepare poly(ethylene terephthalate) polymer.

Poly(ethylene terephthalate) (PET) is generally prepared by contacting an organic ester of terephthalic acid (e.g. dimethyl terephthalate) with ethylene glycol in the presence of an ester exchange catalyst to form bishydroxyethyl terephthalate monomer and then polymerising this monomer to high molecular weight using condensation polymerisation techniques. Various inert additives are introduced during this process, depending on the ultimate use of the polyester. The various manufacturing processes, however, generate considerable waste as the polyester is processed into commercial form. It is known that recycle of waste poly(ethylene terephthalate) would conserve raw materials, improve process economics and elininate the problem of waste disposal.

Several methods are known in the art for recycling of poly(ethylene terephthalate) waste. Such methods mainly consist in recovering the material in the form of spinnable polymer, non-textile end products or monomers. Recovery in the form of spinnable polymer has followed three main routes: In one, poly(ethylene terephthalate) in fiber form is cut to a standard size in a cutting mill, fed to a silo and finally conveyed

to an extruder. The extrudate in the form of a film, band or ribbon is cooled and cut into chips. Alternatively, the melt can be directly used for normal spinning to give continuous filament material (R.Wagner, Fiber Producer, Vol.7, No-2, 1979, P.344 Patent U.K. 1368488). However, during the extrusion melting of the fibrous waste, the polymer undergoes significant thermal, thermo-oxidative and mechanical degradation. Furthermore, the applicability of the process depends strongly upon the quality and form of the waste. For example, waste in the form of lumps and/or chips cannot be recycled by this process.

Another route comprises the conversion of poly (ethylene terephthalate) waste, which is substantially free from severe damage and foreign matter, to powder form. For example, US Patent 1500857 describes a process involving the dissolution of poly(ethylene terephthalate) waste in a suitable solvent, such as naphthalene, which is inert to poly(ethylene terephthalate) and then either its reprecipitation from this solution by means of an antisolvent such as dimethyl formamide or removal of the solvent (naphthalene) at elevated temperature under vacuum. This process yields a polymer which is identical in properties, such as, carboxyl group content, melting point, intrinsic viscosity etc.to the original poly

(ethylene terephthalate) waste. However, such a process requires expensive, highly toxic and hazardous chemicals. The equipment needed for processing the waste and for recovering the solvent is complex. Moreover, it is not easy to convert such ~~six~~ poly (ethylene terephthalate) powder to useful fiber by the normal extrusion processes. Similar processes, but ones using different solvents have been claimed in Patents Czech.171923, Czech.172419, German 2626358 and Ger.2632031.

The third route consists of cutting dry frber waste to short lengths and then extruding it, without melting, through a large orifice e.g. 5mm diameter orifice, to give granules of 5-6 mm length. These granules are melt spun at 290°C and stretched as usual to give useful fiber(Japanese Patent No.7502075) this process is limited to poly(ethylene terephthalate) fibrous waste only. Also, the extrusion of fiber cuttings to granules without melting requires excessively high pressures.

In the recovery of poly(ethylene terephthalate) wasteby conversion to monomers such as dimethyl terephthalate, ethylene glycol, terephthalic acid, bishydroxyethyl terephthalate, or to low molecular weight ethylene terephthalate, the methods generally used comprise methanolysis, glycolysis and hydrolysis. Methanolysis involves the conversion of poly(ethylene terephthalate) waste to dimethyl terephthalate and ethylene glycol

in the presence of methanol at high temperature (180–200°C) and under high pressure (22–40) atm.) and catalysts such as aryl sulphonic acids (US 806269) or acetates of Zn, Na, Mn, Ca, Co etc. (Ludwig 1964). Glycolysis involves the conversion of poly(ethylene terephthalate) waste to bishydroxyethyl terephthalate or low molecular weight ethylene terephthalate in the presence of ethylene glycol at 180–220°C under atmospheric or superatmospheric pressure, and catalysts, such as, acetates of Zn, Na, Mn, Ca, CO, Pb etc. (Indian Pat. 37093), (US Pat. 3830759 and Japanese Patent No. 4078143). Glycolysis may also be followed by methanolysis to get dimethylterephthalate (Ind. Pat. 93424). Hydrolysis involves the conversion of poly(ethylene terephthalate) waste to terephthalic acid in the presence of either a strong mineral acid, such as, sulphuric acid, or water, at high temperature and under pressure (US Pat. 610135). The terephthalic acid obtained thus may be esterified in the presence of methanol to get dimethyl terephthalate (U.S. Pat. 824624).

However, all these three methods for recovery of monomers from poly(ethylene terephthalate) waste are uneconomical as they require a large excess of hazardous or toxic chemicals, under conditions that require high energy consumption. The end products in each case are not in a readily useable condition and need to be

purified before reutilization. In the case of glycolysis, in particular, the use of a large excess of ethylene glycol in the reaction results also in the formation of undesirable ethers, particularly diethylene glycol. The presence of diethylene glycol groups in a polymer obtained from recovered bishydroxyethyl terephthalate is therefore inevitable. Such a polymer results in discoloured fiber possessing reduced melting point, wrinkle resistance and strength, uneven dyeability and increased sensitivity to ultraviolet light.

In view of the aforesaid disadvantages, yet another process has been described in British Patent No.1052927 and which consists in subjecting a molten mixture of a precondensation product of poly(ethylene terephthalate) of low molecular weight and the waste of high molecular weight to the step of continuous polycondensation. Though such a process does obviate certain of the disadvantages described hereinabove, the process of British Patent No.1052927 was itself attended with several disadvantages and limitations.One such limitation was that the step of polycondensation could only be carried out by the principle of falling film evaporation under reduced pressure and at an elevated temperature. Thus, the first stage of the step of polycondensation consisted in treating the melt in a falling film waporator at a temperature of 305°C to 315°C at a pressure of 18 to 25 mm of mercury and,

thereafter, by a second stage at the same temperature but reduced pressure. Yet another limitation was that the prepolymer or the precondensation product was chilled formed into granules and then only mixed with the cut waste and fed into an extruder to form a melt.

Such disadvantages of the known art are avoided by the present invention and, wherein, strangely it has now been found that the prepolymer or precondensation product should be in the form of a melt, when added to the waste, and that the polycondensation is carried by a known batch method of polycondensation and other than by the principle or falling film evaporation.

Accordingly, an object of this invention is to propose an improved process for the preparation of polyethylene terephthalate from polyethylene terephthalate waste.

Another object of this invention is to propose a process for the preparation of polyethylene terephthalate from recycling of polyethylene terephthalate waste wherein, the waste is no longer converted to its monomer.

Yet another object of this invention is to propose a process for the preparation of polyethylene terephthalate from polyethylene terephthalate waste which no longer requires the use of toxic and/or hazardous chemicals.

Still another object of this invention is to propose a process for the preparation of polyethylene terephthalate from polyethylene terephthalate ______________.

waste and, wherein, the undesirable formation of diethylene glycol is eliminated.

A further object of this invention is to propose a process for the preparation of polyethylene terephthalate from waste which does not require the use of any additional expensive or complex equipment.

Further objects and advantages of this invention will be more apparent from the ensuing description.

According to this invention there is provided a process for the preparation of polyethylene terephthalate from polyethylene terephthalate waste which comprises in contacting the waste in any form with a prepolymer of polyethylene terephthalate in a molten state to form a mix, the degree of polymerization of the mix being the average of the degree of polymerization of the prepolymer and waste, homogenizing the mix and then subjecting it to a known step of batch polycondensation.

Thus, in accordance with the present invention, the poly(ethylene terephthalate) waste is no longer reduced to its monomer and, whereby, the disadvantages associated with such a step of reduction and known from the prior art are avoided. Specifically, the waste is now contacted with a prepolymer having a DP of 2 to 60, and preferably, 4 to 10 and where the prepolymer is in a molten state.

Reference is made herein to copending patent application no.87/Del/83 relating to a process for the preparation of copolymers and ~~xx~~ to is lock copolymers of polyethylene terephthalate.

The mix consisting of the prepolymer and waste is maintained...

at a temperature of 200 to 280°C, and preferably between 240 to 260°C, which is homogenized and then subjected to a batch step of polycondensation, and distinct to the continuous falling film evaporator of the known art.

The prepolymer of the said DP range may be prepared for the purpose of contacting it with poly(ethylene terephthalate) waste, the resulting mixture, after homogenization being either polycondensed on its own to any desirable molecular weight or added to the production stream of poly(ethylene terephthalate) at a convenient stage to get useful polymer. Alternatively the prepolymer may be obtained conveniently from the normal production stream of poly(ethylene terephthalate) manufacture. The prepolymer of DP in the said range is drawn off from the stream and brought into contact with poly(ethylene terephthalate) waste, while maintaining it at a temperature in the said range, by either adding it to the poly(ethylene terephthalate) waste in a suitable vessel or adding the poly(ethylene terephthalate) waste to it. The mixture is maintained at this temperature in an inert atmosphere, preferably a nitrogen blanket, till it becomes a homogeneous molten mass. The time required for homogenization may very from 15 min. to 4 hrs., depending upon the prepolymer and poly(ethylene terephthalate) waste compositions, their DP and the physical form of the waste and the temperatures employed. The homogenized mixture of poly(ethylene terephthalate) waste and the poly(ethylene terephthalate)

prepolymer has an average DP that is intermediate between those of the poly(ethylene terephthalate) waste and the poly(ethylene terephthalate) prepolymer.

The ratio of poly(ethylene terephthalate) waste to pre-polymer may very in the range 0.02 to 20.

According to the present process, poly(ethylene terephthalate) waste may be in any form e.g. fibers, chips granules, powder lumps, blocks etc.but preferably not in block form.

The present process is suitable for the recycling of any ethylene terephthalate homopolymer or copolymer waste, in which at least 85 mole percent of the ester units are ethylene terephthalate units. Additional monomeric units in the case of copolymers may be isophthalic acid, 1,4 butandiol and related homologues.

Another important advantage of the present process is that it is suitable for recycling hydrated waste. Hydrated waste is obtained by contacting PET waste with superheated steam (at 350-400°C) in a column and collecting the molten mass in water troughs. The lumps such obtained are crushed in a hammer mill to obtain hydrated waste in granules or powder form. Such waste has low DP and high moisture, and as such is difficult to recycle in transesterification stage. However, in the present process such waste can also be recycled with prepolymer to obtain useful PET polymer.

EXAMPLE-1 :

97 parts of dimethyl terephthalate and 57 parts of ethylene glycol were taken in a reaction vessel provided with a thermometer, a stirrer and a refluxing arrangement. The contents of the vessel were heated to 150°C and then subjected to continuous agitation by means of the stirrer. 5 parts of ethylene glycol containing 0.0441 parts of manganese acetate and 0.00826 parts of sodium acetate were then added to the vessel and the contents heated further to 190°C at which temperature they were maintained for 2.5 hr. The 31 parts of methanol that evolved from the reaction vessel were removed and the temperature of the contents raised slowly to 240°C. 23 parts of ethylene glycol were allowed to evolve from the vessel after which 0.0427 parts of antimony trioxide and 0.07070 parts of triphenyl phosphate were added. The average DP of the resulting prepolymer was 4.

EXAMPLE-2 :

1 part of waste poly(ethylene terephthalate) fibers of average DP 90 which was compressed in presence of steam to a compact mass was gradually brought into contact with 1 part of the prepolymer maintained at 240°C. The temperature of the mixture was raised gradually to 260°C while the contacting was taking place. The mixture was then allowed to homogenize at this temperature. The homogenization was complete in 45 min. The average DP of

the mixture was 37. The mixture was then subjected to polycondensation conditions as follows: The temperature of the mixture was maintained at 260°C initially. The pressure over the mixture was reduced gradually from 760 torr to 0.8-1 torr over a period of 90 min. During this period the temperature of the mixture was raised gradually to 280°C. The polycondensation reaction was allowed to proceed under these conditions for 3.0 hr. The melting point of the polymer obtained thus was found to be 260°C and the intrinic viscosity at 20°C of a 0.5% solution of the polymer in a 1:1 mixture of phenol and tetrachloroethane was 0.66. These values for melting point and intrinsic viscosity compare favourably with 260°C and 0.66 respectively for a polymer obtained normally from virgin monomer.

In another example same conditions as in Example 2 were maintained except that 1.5 parts of poly(ethylene terephthalate) chips of average DP 100 were used instead of 1 part of poly(ethylene terephthalate) fiber of average DP 90. The resulting homogeneous mixture had a DP of 55 and polycondensing it as described in Example 2 the resulting polymer has a melting point of 260°C and an intrinsic viscosity of 0.66.

In another example 1 part of poly(ethylene terephthalate) fiber of average DP 90 in Example 2 were replaced by 2 parts of poly(ethylene terephthalate) chips of

average DP 100 keeping all other conditions same. The resulting homogeneous mixture had an average DP of 62 and subsequent polymer obtained from it had a melting point of 260°C and an intrinsic viscosity of 0.66.

EXAMPLE-3 :

PET waste is fiber, lumps, chips form was counter-currently contacted with superheated steam at 350°C in a vertical column. Waste was charged from the top and the steam from the bottom. The resulting molten mass was quenched in water trough and the lumps hydrated PET waste thus obtained was crushed in hammer mill to obtain ~~xx~~ powdered hydrated waste.

1 part of such hydrated waste was used instead of 1 part PET fibers in Example 2. Same procedure was repeated and the final product obtained after poly-condensation was comparable in color and other properties with the polymer obtained normally from virgin monomers.

WE CLAIM : 158902

1) A process for the preparation of polyethylene terephthalate from polyethylene terephthalate waste which comprises in contacting the waste in any form with a prepolymer of polyethylene terephthalate in a molten state to form a mix, the degree of polymerization of the mix being the average of the degree of polymerization of the prepolymer and waste, homogenizing the mix and then subjecting it to a ~~batch~~ known step of batch polycondensation.

2) A process as claimed in claim 1 wherein the mix consisting of the waste and the prepolymer is homogenized at a temperature of 200 to 280°C.

3) A process as claimed in claim 2 wherein the mix is homogenized at a temperature of 240 to 260°C.

4) A process as claimed in claim 1 wherein the waste is in any form, such as fibres, chips, granules or powder lumps.

5) A process as claimed in claim 1 wherein the prepolymer has a DP of 2 to 100 and, preferably, 4 to 10.

6) A process as claimed in claim 1 wherein the mix is maintained in an inert atmosphere during the step of homogenization.

158902

7) A process for the preparation of polyethylene terephthalate from polyethylene terephthalate waste substantially as herein described and exemplified in the examples.

Dated this 11th day of FEBRUARY, 1983.

(G.S. DAVAR)
of L.S. DAVAR & CO.
Applicants' Attorney.